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Photochemical Production of H_2SO_4 Aerosols on Venus

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FINAL TECHNICAL REPORT

Evidence for SO_2 injection (by a volcano?) into the upper atmosphere
of Venus

The quantum yields for producing $\text{O}_2(a^1\Delta_g)$ and $\text{O}_2(b^1\Sigma_g^+)$ for reaction (3) are summarized in Table I which also includes results for other simple reactions capable of producing the singlet oxygen states. In general, the quantum yields are very small, ranging from less than 10^{-4} to 4×10^{-2} .

According to Yung and DeMore (1982), the $\text{O}_2(a^1\Delta_g)$ emissions due to (1), (2), and (3) could be as high as 0.72, 0.37, and 0.72 MR, respectively, adding up to a total of 1.8 MR, if the quantum yields for forming $\text{O}_2(a^1\Delta_g)$ in the reactions were unity. However, using the current values for quantum yields, we obtain revised estimates of $\text{O}_2(a^1\Delta_g)$ emission (including cascading from $\text{O}_2(b^1\Sigma_g^+)$) due to (1), (2), and (3) as 0.029, 0.007, and 0.014 MR, respectively. The total amounts to 0.05 MR, considerably less than the observed 1.2-1.5 MR.

We now face a fundamental dilemma. Reaction (1) turns oxygen atoms into O_2 . Reactions (2) and (3) constitute a catalytic cycle for converting odd oxygen into O_2 . The ultimate source of O atoms in the upper atmosphere of Venus in the present model is CO_2 photolysis, which proceeds at a mean rate of $8 \times 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$. This implies that the total rate of O-O bond formation cannot exceed $4 \times 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$. Therefore, if the quantum yield for producing the $a^1\Delta_g$ state is q in each O-O bond forming reaction, the airglow would be less than $4q$ MR. The recent laboratory results suggest that q is a few percent or less. Hence, the $\text{O}_2(a^1\Delta_g)$ emission of Venus cannot arise from O-O bond

forming reactions in which the O atoms are derived from CO_2 dissociation. The simplicity of the argument outlined here suggests that our conclusion is largely independent of the details of the photochemical model.

One obvious possibility is that there might have been a calibration error in the observations. A discussion with one of the authors (Traub, 1987, private communication) led to a critical re-examination of the data analysis procedure used in Connes et al.'s (1979) paper. It was concluded that calibration errors could have been at most a factor of 2, since two independent methods, based on the terrestrial airglow and the Venus continuum brightness were used, and both methods gave essentially the same result.

We can speculate on other explanations. The crucial clue is the source of O atoms. As was first pointed out by Winnick and Stewart (1980), photolysis of SO_2 is a major source of O atoms in the stratosphere of Venus. Indeed, according to the models of Winnick and Stewart (1980), and Yung and DeMore (1982), the photolysis rate of SO_2 on Venus is considerably higher than that of CO_2 . However, most of the photolysis of SO_2 occurs in the lower part of the stratosphere, just above the cloud tops (~ 60 km). Any $\text{O}_2(a^1\Delta_g)$ produced in this region would be effectively quenched, and could not contribute to the observed emissions under "normal" circumstances.

Consider now an unusual event, an episodic injection of SO_2 into the upper atmosphere of Venus. We shall leave the cause of this event unspecified, although volcanism is a possibility (Esposito, 1984). The presence of large quantities of SO_2 in the upper stratosphere (above 80 km) would lead to rapid photolysis and production of oxygen atoms. Recombination of these atoms either by (1) or the catalytic cycle (2) and (3) would yield a source of $\text{O}_2(a^1\Delta_g)$. Detailed modeling of this event appears difficult since the $\text{O}_2(a^1\Delta_g)$ airglow observations were carried out in 1975, before there were any quantitative data on SO_2 (Pioneer-Venus started collecting data in 1978).

Table I

List of the relevant reactions that produce $O_2(a^1\Delta_g)$ and $O_2(b^1\Sigma_g^+)$ in the atmosphere of Venus and their quantum yields.

	Reactions	Quantum Yield [*]		References
		$O_2(a)$	$O_2(b)$	
1	$O + O + M \rightarrow O_2 + M$	4(-2)	2(-2)	Wraight
			3(-2)	Ogryzlo et al.
			4(-5)	Young and Black
2	$Cl + O_3 \rightarrow ClO + O_2$	<2(-2)	<5(-4)	Choo and Leu
3	$O + ClO \rightarrow Cl + O_2$	<2.5(-2)	4.4(-4)	This work
4	$Cl + ClO_2 \rightarrow Cl_2 + O_2$	1.4(-2)	6(-3)	Choo and Leu
5	$Cl + HO_2 \rightarrow HCl + O_2$		<5(-4)	Keyser et al.
6	$H + HO_2 \rightarrow H_2 + O_2$	1.5(-2)		Washida et al.
			2.8(-4)	Hislop and Wayne
			<1(-2)	Keyser et al.
7	$O + HO_2 \rightarrow OH + O_2$		<8(-3)	Keyser et al.

* Defined as the rate coefficient for the branch divided by the total rate coefficient.

Determination of $O_2(a^1\Delta_g)$ and $O_2(b^1\Sigma_g^+)$ Yields in the
Reaction $O + ClO \rightarrow Cl + O_2$: Implications for Photochemistry
in the Atmosphere of Venus

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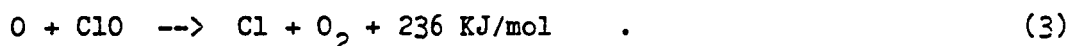
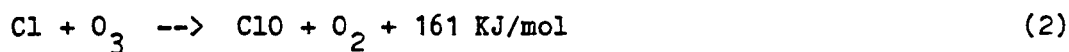
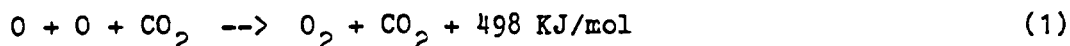
Contribution number 4465 from the Division of Geological and Planetary Sciences,
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Abstract

A discharge flow apparatus with a chemiluminescence detector has been used to study the reaction $O + ClO \rightarrow Cl + O_2^*$, where $O_2^* = O_2(a^1\Delta_g)$ or $O_2(b^1\Sigma_g^+)$, and the radiative decay of O_2^* . The measured quantum yields for producing $O_2(a^1\Delta_g)$ and $O_2(b^1\Sigma_g^+)$ in the above reaction are less than 2.5×10^{-2} and $(4.4 \pm 1.1) \times 10^{-4}$, respectively. The observed $O_2(a^1\Delta_g)$ airglow of Venus cannot be explained in the context of standard photochemistry using our experimental results and those reported in recent literature. The possibility of an episodic injection of SO_2 into the mesosphere of Venus is speculated.

Introduction

The intense $O_2(a^1\Delta_g)$ emission of Venus at $1.27 \mu m$ was discovered by Connes et al. (1979), who estimated the dayglow and nightglow brightness to be 1.5 and 1.2 MR (1 Megarayleigh = 1×10^{12} photons $cm^{-2} s^{-1}$), respectively. The aforementioned authors also proposed that the most likely processes for producing $O_2(a^1\Delta_g)$ on Venus are:



Detailed modeling by Yung and DeMore (1982) and Krasnopolsky and Parshev (1983) showed that, in order to explain the Venus observations, the quantum yields in reactions (1)-(3) must be close to unity.

Reaction (1) has been studied by a number of workers (see recent review by Wayne, 1985). The quantum yields for singlet oxygen (both a and b states), as summarized in Table III, are low. Reaction (2) was studied by Choo and Leu (1985), who found no evidence for the production of excited O_2 (see Table III). In this article we shall report new experimental results on the quantum yields of singlet oxygen produced by reaction (3). Using the known efficiencies for producing $O_2(a^1\Delta_g)$ in (1)-(3), we can make a quantitative comparison of the modeled and observed airglow brightness of Venus. The results will be briefly discussed.

Experiment

The experimental technique used in this study has been described in detail in previous publications (Leu, 1984; Choo and Leu, 1985). The production and detection of the single oxygen molecules, $O_2(a^1\Delta_g)$ and $O_2(b^1\Sigma_g^+)$, were carried out in a discharge flow apparatus with a chemiluminescence detector.

Oxygen atoms were produced in the side arm of the flow tube via the fast reaction



where the nitrogen atoms were generated in a microwave discharge by passing nitrogen gas through a quartz tube. Since the N atoms were slightly in excess, the final O atom concentration would be equal to that of NO, which was measured with a mass flowmeter.

ClO radicals were generated as follows: First, Cl atoms in the concentration range $(5-10) \times 10^{13} \text{ cm}^{-3}$ were produced by passing a small amount of Cl_2 in a helium carrier through a microwave discharge tube. Then, Cl atoms, in slight excess, were allowed to react with Cl_2O in a fast reaction leading to the production of ClO



The Cl_2O molecules used in this work were prepared as described in Leu (1984). The absolute concentration of Cl_2O was monitored by an optical absorption technique. The light source was a low pressure mercury lamp, which emits a strong line at 253.7 nm, and the adopted cross section for Cl_2O at this wavelength is $2.01 \times 10^{-18} \text{ cm}^2$. The detector was a photomultiplier equipped

with an interference filter. By virtue of the stoichiometry of reaction (5), the final concentration of ClO must equal the initial concentration Cl_2O . Having prepared the ClO molecules in this manner, they were then introduced into the reaction cell via a movable Pyrex injector.

The observation of the singlet oxygen emissions was carried out using the chemiluminescence detection system. Radiation in the wavelength range 600-900 nm was resolved with a 1/4 m McPherson monochromator (Model 275) and registered by a Hamamatsu cooled photomultiplier tube (Model R943-02) in conjunction with a Keithley picoammeter (Model 480). Radiation in the wavelength range 900-1700 nm was resolved with an Oriel grating monochromator (Model 7240) and detected with a liquid nitrogen cooled germanium detector (Applied Detector Corp. Model 403L). The signals were modulated with a 100 Hz chopper (Bulova) and a lock-in amplifier (EG & G Model 5804) was used for the phase sensitive detection. Detection of emissions from both singlet oxygen states were simultaneously recorded on a two-channel recorder.

Figure 1 shows the chemiluminescence data taken under the following conditions: $[\text{O}] = [\text{ClO}] = 1.7 \times 10^{13} \text{ cm}^{-3}$ ($[x]$ denotes the concentration of species x); total pressure = 1.25 Torr; flow velocity = 3620 cm s^{-1} ; and reaction time = 4.8 ms. $\text{O}_2(b^1\Sigma_g^+)$ emission at 762 nm with a bandwidth of 10 nm was clearly detected. This result suggests that there were $3.8 \times 10^9 \text{ cm}^{-3}$ of O_2 in the $b^1\Sigma_g^+$ state, derived from reaction (3). $\text{O}_2(a^1\Delta_g)$ emission at 1270 nm was not detectable in the same experiment. The experimental data are summarized in Table I. In order to derive the quantum yields of $\text{O}_2(a^1\Delta_g)$ and $\text{O}_2(b^1\Sigma_g^+)$, it is necessary to employ a computer simulation. The set of relevant chemical reactions is listed in Table II. The rate of loss of $\text{O}_2(b^1\Sigma_g^+)$ on the walls of the reaction cell and quenching by N_2 has been

measured using the same technique as reported here. The rate of loss of $O_2(a^1\Delta_g)$ by quenching on the walls and by collisions with N_2 , Cl , O , and ClO can be shown to be negligible. The experimental conditions have been chosen so as to minimize interference from the reactions (1) and $Cl + ClO_2 \rightarrow Cl_2 + O_2$. The results of our analysis can be summarized as: $k_a < 9 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$, and $k_b = (1.6 \pm 0.4) \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$ for the absolute rate constants for (3) to produce $O_2(a^1\Delta_g)$ and $O_2(b^1\Sigma_g^+)$, respectively. The uncertainty represents one standard deviation error.

Discussion

The quantum yields for producing $O_2(a^1\Delta_g)$ and $O_2(b^1\Sigma_g^+)$ for reaction (3) are summarized in Table III, which also includes results for other simple reactions capable of producing the singlet oxygen states. In general, the quantum yields are very small, ranging from less than 10^{-4} to 4×10^{-2} .

According to Yung and DeMore (1982), the $O_2(a^1\Delta_g)$ emissions due to (1), (2), and (3) could be as high as 0.72, 0.37, and 0.72 MR, respectively, adding up to a total of 1.8 MR, if the quantum yields for forming $O_2(a^1\Delta_g)$ in the reactions were unity. However, using the current values for quantum yields, we obtain revised estimates of $O_2(a^1\Delta_g)$ emission (including cascading from $O_2(b^1\Sigma_g^+)$) due to (1), (2), and (3) as 0.029, 0.007, and 0.014 MR, respectively. The total amounts to 0.05 MR, considerably less than the observed 1.2-1.5 MR.

We now face a fundamental dilemma. Reaction (1) turns oxygen atoms into O_2 . Reactions (2) and (3) constitute a catalytic cycle for converting odd oxygen into O_2 . The ultimate source of O atoms in the upper atmosphere of Venus in the present model is CO_2 photolysis, which proceeds at a mean rate of $8 \times 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$. This implies that the total rate of O-O bond formation cannot exceed $4 \times 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$. Therefore, if the quantum yield for producing the $a^1\Delta_g$ state is q in each O-O bond forming reaction, the airglow would be less than $4q$ MR. The recent laboratory results suggest that q is a few percent or less. Hence, the $O_2(a^1\Delta_g)$ emission of Venus cannot arise from O-O bond forming reactions in which the O atoms are derived from CO_2 dissociation. The simplicity of the argument outlined here suggests that our conclusion is largely independent of the details of the photochemical model.

One obvious possibility is that there might have been a calibration error in the observations. A discussion with one of the authors (Traub, 1987, private communication) led to a critical re-examination of the data analysis procedure used in Connes et al.'s (1979) paper. It was concluded that calibration errors could have been at most a factor of 2, since two independent methods, based on the terrestrial airglow and the Venus continuum brightness were used, and both methods gave essentially the same result.

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Conclusion

A discharge flow apparatus with a chemiluminescence detector has been used to determine the quantum yields of $O_2(a^1\Delta_g)$ and $O_2(b^1\Sigma_g^+)$ in the reaction $O + ClO \rightarrow Cl + O_2$. The results are summarized in Tables II and III. Application of these results to explain the airglow brightness of Venus reveals a fundamental difficulty with a "normal" photochemical model. The upper atmosphere of Venus might have been strongly perturbed by a massive injection of SO_2 in 1975.

It is important that our laboratory kinetics-chemiluminescence results be confirmed using an independent experimental technique. The $O_2(a^1\Delta_g)$ emission from Venus have been observed only once. These observations should be repeated to establish the magnitude and nature of possible variations, along with the simultaneous observation of other chemical species such as CO, H_2O , HCl, HF, O_2 , and SO_2 .

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Table I.
Summary of $O_2(b^1\Sigma_g^+)$ Measurements⁺

[O] (cm ⁻³)	[ClO] (cm ⁻³)	Reaction Time (ms)	[O ₂ (b)] (cm ⁻³)	k _b [*] (cm ³ s ⁻¹)	Number of Experiments
1.5(13)	4.9(12)	3.0	1.0(9)	1.2(-14)	1
1.5(13)	1.6(13)	3.0	2.8(9)	1.3(-14)	1
1.6(13)	1.1(13)	4.8	3.4(9)	1.9(-14)	3
1.6(13)	1.6(13)	4.8	3.6(9)	1.6(-14)	2
1.6(13)	1.7(13)	4.8	3.8(9)	1.4(-14)	6
1.6(13)	1.9(13)	4.8	5.2(9)	2.1(-14)	1
Average Value (1.6 ± 0.4) x (-14) ^{**}					

⁺The numbers a(b) should be read as a x 10^{-b} in this table and Tables II and III.

^{*}Best fit of the $O_2(b^1\Sigma_g^+)$ measurement.

^{**}One standard deviation.

Table II.

Chemical scheme for computer simulation of the production of $O_2(a^1\Delta_g)$ and $O_2(b^1\Sigma_g^+)$ in the reaction $O + ClO \rightarrow Cl + O_2$

Reactions	Rate Constant ($cm^3 s^{-1}$)	References
$O + ClO \rightarrow Cl + O_2$	$3.6(-11)$	Leu
$Cl + O_2(a)$	$<9.0(-13)$	This work
$Cl + O_2(b)$	$1.6(-14)$	"
$O_2(a) + wall \rightarrow O_2$	0	Choo and Leu
$O_2(a) + N_2 \rightarrow O_2 + N_2$	$1.0(-19)$	"
$O_2(a) + Cl \rightarrow O_2 + Cl$	$1.0(-16)$	*
$O_2(a) + O \rightarrow O_2 + O$	$1.0(-16)$	*
$O_2(a) + ClO \rightarrow O_2 + ClO$	$1.0(-16)$	*
$O_2(b) + wall \rightarrow O_2$	80.0	Choo and Leu
$O_2(b) + N_2 \rightarrow O_2 + N_2$	$1.7(-15)$	"
$O_2(b) + Cl \rightarrow O_2 + Cl$	$1.0(-13)$	*
$O_2(b) + O \rightarrow O_2 + O$	$1.0(-13)$	*
$O_2(b) + ClO \rightarrow O_2 + ClO$	$1.0(-13)$	*

* Estimated based on analogous reactions; see the review by Wayne (1985).

Table III

List of the relevant reactions that produce $O_2(a^1\Delta_g)$ and $O_2(b^1\Sigma_g^+)$ in the atmosphere of Venus and their quantum yields.

Reactions	Quantum Yield [*]		References
	$O_2(a)$	$O_2(b)$	
$O + O + M \rightarrow O_2 + M$	4(-2)	2(-2)	Wraight
		3(-2)	Ogryzlo et al.
		4(-5)	Young and Black
$Cl + O_3 \rightarrow ClO + O_2$	<2(-2)	<5(-4)	Choo and Leu
$O + ClO \rightarrow Cl + O_2$	<2.5(-2)	4.4(-4)	This work
$Cl + ClO_2 \rightarrow Cl_2 + O_2$	1.4(-2)	6(-3)	Choo and Leu
$Cl + HO_2 \rightarrow HCl + O_2$		<5(-4)	Keyser et al.
$H + HO_2 \rightarrow H_2 + O_2$	1.5(-2)		Washida et al.
		2.8(-4)	Hislop and Wayne
		<1(-2)	Keyser et al.
$O + HO_2 \rightarrow OH + O_2$		<8(-3)	Keyser et al.

* Defined as the rate coefficient for the branch divided by the total rate coefficient.

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Figure Caption

Figure 1. Chemiluminescence spectra taken from the reaction of atomic oxygen with ClO radical (see text for detail).

